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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Polyisocyanates Containing Hydroxyl and Uretdione Groups

(72) Gras, Rainer - Germany (Federal Republic of) ;

(71) Hüls Aktiengesellschaft - Germany (Federal Republic of)
;

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Notice: This application is as filed and may therefore contain an incomplete specification.



ABSTRACT

Disclosed are polyaddition products containing hydroxyl groups and uretdione groups, and essentially comprising

A) from 55 to 85% by weight of a uretdione, and at least one of:

B) from 2 to 15% by weight of a polyol with ≥ 3 hydroxyl groups,

C) from 5.5 to 31% by weight of a diol,

D) from 7.5 to 33% by weight of a chain extender with a functionality of ≥ 2 to ≤ 6 ,

provided that when the polyol B is not contained, the chain extender D with a functionality of ≥ 3 must be contained,

wherein the polyisocyanates carry terminal hydroxyl groups and have a functionality of ≥ 3 , a molecular weight between 1,500 and 4,400 and a free isocyanate content of less than 0.5% by weight. The polyaddition products are useful as components of polyurethane powder coating compositions.

The invention relates to polyaddition products containing hydroxyl groups and uretdione groups and having a functionality of at least 3, and to a process for their preparation and use for the preparation of polyurethane (PU) polymers, especially of elimination-free PU coating systems, very preferably of PU powder coating systems, and to the PU coatings prepared thereby.

10 Polyisocyanates for use in polyurethane powder coatings, containing uretdione groups, are known in particular from German Patent Publication (DE-A) 30 30 554. Such polyisocyanates, however, have only two terminal, partially or completely blocked isocyanate groups and are strictly linear in structure. As revealed by European Patent Publication (EP-A)-254 152 (page 2, column 1, line 63 to end of sentence), this state of affairs is of great disadvantage in practice.

20 Described in EP-A-639 598 is a method based on the polyaddition reaction of polyisocyanates containing uretdione groups with diols and/or with bifunctional chain extenders and, as evident from the examples, with monoalcohols. Owing to the use of monoalcohols, even the use of polyisocyanate-uretdiones containing isocyanurate groups and having more than two NCO functions does not lead to more highly functionalized polyaddition products, the crosslinking agents for PU powder coatings. However, as mentioned above, this is a disadvantage for the quality of the coating.

In accordance with DE-A 19 505 566, it was possible for the first time to employ polyols having more than two

hydroxyl groups for the preparation of the claimed polyisocyanates containing uretdione groups. However, for this purpose it was necessary to first partially block the isocyanate groups of the polyisocyanate-uretdiones in order to avoid gelling. For economic reasons, removable blocking agents were employed. This, however, constitutes an ecological disadvantage.

10 A major object of the present invention, therefore, is to provide polyisocyanates containing uretdione groups, in order to use these crosslinking agents for the preparation of elimination-free PU polymers, especially of PU powder coatings, and the PU powder coatings prepared thereby, which no longer have the stated disadvantages of the prior art.

The present invention accordingly provides polyaddition products which contain hydroxyl groups and uretdione groups and consist essentially of:

- A) from 55 to 85% by weight of uretdiones derived from diisocyanates, and at least one hydroxyl compound selected from the group consisting of:
- 20 B) from 2 to 15% by weight of polyols having at least 3 hydroxyl groups,
- C) from 5.5 to 31% by weight of diols, and
- D) from 7.5 to 33% by weight of chain extenders having a functionality of from 2 to 6, provided that when the polyols B) are not contained, then the chain extenders D) having at least 3 hydroxyl groups must be contained, whereby the polyaddition products carry terminal hydroxyl groups and have a

functionality of three or more, preferably from three to four, a molecular weight of between 1,500 and 4,400, preferably between 1,800 and 3,500, and a free isocyanate content of less than 0.5% by weight. The polyaddition products may also be called as polyisocyanates hereinunder since they are derived from diisocyanates, although they contain essentially no free isocyanate groups.

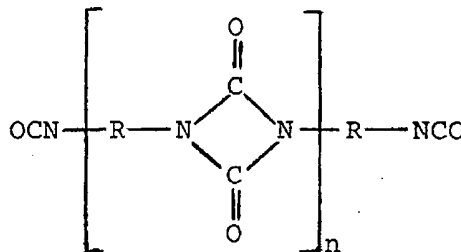
10 The invention additionally provides the use of the polyisocyanates containing hydroxyl groups and uretdione groups for the preparation of polyurethane (PU) polymers, especially in combination with hydroxyl-containing polymers, in elimination-free, transparent and pigmented polyurethane (PU) powder coatings of increased network density, very good reactivity and excellent gloss, and also provides elimination-free transparent and pigmented polyurethane (PU) powder coatings comprising the polyisocyanates according to the invention, containing hydroxyl groups and uretdione groups and having a functionality of at least 3.

20 The uretdiones employed in accordance with the invention (component A) are obtained from diisocyanates in accordance with the known methods, and it is possible, in principle, to employ all known diisocyanates.

Preferred uretdiones, however, are derived from diisocyanates selected from the group consisting of hexamethylene 1,6-diisocyanate (HDI), 2-methylpentamethylene 1,5-diisocyanate (DI 51), 2,2,4(2,4,4)-trimethylhexamethylene diisocyanate and isophorone diisocyanate (IPDI). These

diisocyanates may be employed individually or in mixtures as component A.

Typical uretdiones derived from diisocyanates have terminal isocyanate groups and may be represented by the formula:



wherein n is an integer such as 1 to 6 and R is the residue of the diisocyanate.

10 Particularly preferred is the uretdione of isophorone diisocyanate.

The typical isocyanurate-free uretdione of isophorone diisocyanate (IPDI) is highly viscous at room temperature, i.e. the viscosity is greater than 10^6 mPa·s; at 60°C, it is 13×10^3 mPa·s and at 80°C, it is 1.4×10^3 mPa·s. The free NCO content is between 16.8 and 18.5% by weight; in other words, more or less high proportions of polyuretdione of IPDI must be present in the reaction product. The monomer content is about 1% by weight. The overall NCO content of the reaction product after heating at 180 - 200°C is 37.5 - 37.8% by weight.

20 When conventional catalysts and processes are used to dimerize aliphatic diisocyanates, isocyanurates are often formed as by-products in varying quantities, so that the NCO

functionality of the isocyanurate-containing polyisocyanate-uretdiones employed is usually from about 2 to about 2.5. It is therefore highly surprising that isocyanurate-containing polyisocyanate-uretdiones of this type can be employed for the synthesis of polyisocyanates containing hydroxyl groups and uretdione groups and having a functionality of at least 3 without the occurrence of gelling.

Suitable polyols (component B) in accordance with the invention preferably have three to six hydroxyl groups and examples thereof include glycerol, trimethylolpropane, ditrimethylolpropane, trimethylolethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β -hydroxyethyl) isocyanurate, pentaerythritol, mannitol and sorbitol, with preference being given to the use of trimethylolethane, trimethylolpropane (TMP) and trishydroxyethyl isocyanurate (THEIC). They are used individually or in mixtures.

The diols employed in accordance with the invention (component C) include all those customarily employed in PU chemistry. Examples of particularly preferred diols include: ethylene glycol (E), triethylene glycol (TEG), 1,4-butanediol (B), 1,5-pentanediol (P), 1,6-hexanediol (HD), 3-methyl-1,5-pentanediol (Pm), neopentylglycol (N), 2,2,4(2,4,4)-trimethylhexanediol (T) and neopentylglycol hydroxypivalate (Eg).

The novel polyisocyanates may also contain chain extenders (component D) having a functionality of from 2 to 6, in particular from 2 to 4, in the form of linear and branched

hydroxyl-terminated polyesters having a molecular weight of between 180 and 2,000, preferably between 230 and 1,500, and a hydroxy number of between 900 and 50 mg of KOH/g, preferably between 700 and 100 mg of KOH/g. They are prepared, for example, by condensing polyols (e.g., diols) and dicarboxylic acids or by polymerizing lactones or hydroxycarboxylic acids. The "chain extenders" here generally mean oligomers and low polymerization polymers having terminal hydroxyl groups.

10 Preferred chain extenders used are linear, hydroxyl-terminated polyesters or polycaprolactones having a molecular weight of between 180 and 2,000 and a hydroxyl number of between 625 and 50 mg of KOH/g.

Other preferred chain extenders used are branched polyesters or polycaprolactones having a functionality of 3 to 6, a molecular weight between 210 and 2,000 and a hydroxyl number between 900 and 100 mg of KOH/g.

20 To prepare the chain extenders, it is preferred to employ the abovementioned polyols and/or diols, supplemented by 2-methyl-1,3-propanediol, diethylene glycol, 1,12-dodecanediol and trans- and cis-cyclohexanedimethanol (CHDM).

The preferred dicarboxylic acids include aliphatic acids with or without alkyl branching, such as succinic acid, adipic acid (As), suberic, azelaic and sebacic acid (Sb), 2,2,4(2,4,4)-trimethyladipic acid.

Alternatively, the chain extenders may be prepared by polymerizing lactones and hydroxycarboxylic acids, such as ϵ -caprolactone and hydroxycaproic acid. These lactones and

hydroxycarboxylic acids may further be used by partly replacing the dicarboxylic acid or the diols.

The hydroxyl-containing reactants, namely components B, C and D, are employed such that the OH component necessarily contains at least one of the polyol B and the chain extender D having three or more OH groups. In a preferred embodiment, at least one mol of the polyols B or the chain extenders having three to OH groups per three mols of the uretdiones A may be employed.

10 The mixing ratio of the hydroxyl-containing reactants (i.e., B, C and D) with the uretdione must be chosen such that the functionality of the polyaddition products is at least 3.

The polyaddition products according to the invention can be obtained preferably by the process described as follows.

The reaction in solvent takes place in general at temperatures from 50 to 100°C, preferably between 60 and 90°C. The OH component (one or more of the polyol B, diol C and chain extender D) is initially introduced into a reaction vessel, and the uretdione is added as rapidly as possible
20 keeping the reaction temperature within the abovementioned limits. The reaction is complete after from 30 to 150 minutes. The solvent is then removed, suitably using evaporation screws, filmtruders or spray dryers.

Suitable solvents include benzene, toluene or other aromatic or aliphatic hydrocarbons, acetates such as ethyl acetate or butyl acetate, ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, or chlorinated aromatic and

aliphatic hydrocarbons, and any desired mixtures of these or other inert solvents.

The invention additionally provides the solvent-free and continuous preparation of the addition products by means of intensive kneading apparatus in a single-screw or multi-screw extruder, in particular in a twin-screw extruder. The solvent-free synthesis requires temperatures of from 110 to 190°C. It was surprising that such high temperatures can be used for the uretdione syntheses. These temperatures are
10 already well within the recleaving range for uretdiones, with the possibility that high free isocyanate contents may result, whereby uncontrolled reaction processes might be expected. This factor was significant for the synthesis of the hydroxyl-containing uretdione polyaddition product, and it was all the more surprising that the synthesis could be carried out. A factor which proved to be of advantage here was the short reaction times of less than 5 minutes, preferably less than 3 minutes, in particular less than 2 minutes.

Another matter of significance is that the short-
20 term exposure to heat is sufficient in order to mix the reactants homogeneously, during which they are completely or extensively converted. The batch is subsequently cooled in a controlled manner, in accordance with the establishment of equilibrium, and, if necessary, the conversion is completed (by further heating).

The reaction substrates are fed to the reaction kneading apparatus in separate substrate streams, it being

possible for the starting components to be preheated at up to 120°C, preferably up to 90°C. Where there are more than two product streams, they can also be added together. Polyol and/or diol and/or chain extenders and/or catalysts and/or further customary paint additives, such as leveling agents and/or stabilizers, can be brought together to form one product stream; the same applies to those components which are inert towards isocyanate groups; catalysts and abovementioned paint additives.

10 The sequence of the substrate streams can also be varied, as can the point of entry of the substrate streams.

For after-reaction, cooling, comminution and bagging, known techniques and technologies are used.

In order to accelerate the polyaddition reaction it is also possible to use catalysts which are customary in polyurethane chemistry, which are employed in a concentration of from 0.01 to 1% by weight, preferably from 0.03 to 0.5% by weight, based on the reaction components employed. Compounds which have proven particularly suitable to date are tin(II) and tin(IV) compounds. Particular mention is made here of dibutyltin dilaurate (DBTL). However, other catalysts should not be regarded as being unsuitable in principle.

The present invention provides, furthermore, for the use of polyisocyanates containing hydroxyl groups and uretdione groups for the preparation of polyurethane polymers, especially in combination with hydroxyl-containing polymers and/or the additives which are customary in polyurethane chemistry, for the preparation of elimination-free, transparent and pigmented PU powder coatings which are distinguished by very good reactivity and are therefore both economically and ecologically significant, and which surprisingly, despite increased network density, are of outstanding flexibility.

The present invention also provides elimination-free PU powder coatings consisting of the polyisocyanates according to the invention in combination with hydroxyl-containing polymers. Suitable co-reactants for PU powder

coatings are compounds which carry functional groups which, during the curing process, react with isocyanate groups as a function of temperature and time, examples being hydroxyl, carboxyl, mercapto, amino, urethane and
5 (thio)urea groups. Polymers which can be employed are addition polymers, condensation polymers and polyaddition compounds.

Preferred components are primarily polyethers, polythioethers, polyacetals, polyesteramides, epoxy resins with
10 hydroxyl groups in the molecule, amino resins and their modification products with polyfunctional alcohols, polyazomethines, polyurethanes, polysulfonamides, melamine derivatives, cellulose esters and cellulose ethers, partially hydrolyzed homo- and copolymers of
15 vinyl esters, but especially polyesters and acrylate resins.

Preferred carboxylic acids for the preparation of polyesters can be aliphatic, cycloaliphatic, aromatic and/or heterocyclic in nature and may if desired be
20 substituted by halogen atoms and/or may be unsaturated. Examples thereof are succinic, adipic (As), suberic, azelaic, sebacic, phthalic, terephthalic (TS), isophthalic (Is), trimellitic, pyromellitic, tetrachlorophthalic, endomethylenetetrahydrophthalic, glutaric,
25 maleic and fumaric acids and - where obtainable - their anhydrides, dimethyl terephthalate (DMT), bisglycol terephthalate, and also cyclic monocarboxylic acids, such as benzoic acid, p-tert-butylbenzoic acid and hexahydro-

benzoic acid.

Examples of suitable polyhydric alcohols are ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol, di- β -hydroxyethylbutanediol, 1,6-hexanediol, 5 diol, 1,8-octanediol, neopentylglycol, cyclohexanediol, 1,4-bis(hydroxymethyl)cyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, 2,2-bis[(β -hydroxyethoxy)phenyl]propane, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 2,2,4(2,4,4)-trimethyl-1,6-hexanediol, glycerol, 10 trimethylolpropane, trimethylolethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β -hydroxyethyl) isocyanurate, pentaerythritol, mannitol and sorbitol and also diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polypropylene glycols, polybutylene 15 glycols, xylylene glycol and neopentylglycol hydroxypivalate.

It is also possible to employ mono- and polyesters as lactones, for example ϵ -caprolactone, or hydroxycarboxylic acids, for example hydroxypivalic acid, ω -hydroxy- 20 decanoic acid, ω -hydroxycaproic acid, thioglycolic acid. Polyesters of the abovementioned polycarboxylic acids and/or their derivatives and polyphenols, such as hydroquinone, bisphenol A, 4,4'-dihydroxybiphenyl or bis(4-hydroxyphenyl) sulfone; polyesters of carbonic acid 25 which are obtainable from hydroquinone, diphenylolpropane, p-xylylene glycol, ethylene glycol, butanediol or 1,6-hexanediol and other polyols by customary condensation reactions, for example with phosgene or with

diethyl or diphenyl carbonate, or from cyclic carbonates such as glycol carbonate or vinylidene carbonate, by polymerization in a known manner; polyesters of silicic acid, polyesters of phosphoric acid, for example of methane-, ethane-, β -chloro-ethane-, benzene- or styrene-phosphoric acid, -phosphoryl chloride or -phosphoric ester and polyalcohols or polyphenols of the abovementioned type; polyesters of boric acid; polysiloxanes, for example the products obtainable by hydrolysis of dialkyldichlorosilanes with water and subsequent treatment with polyalcohols, and those obtainable by addition of polysiloxane dihydrides onto olefins, such as allyl alcohol or acrylic acid.

Preferred polyesters are also for example the reaction products of polycarboxylic acids and glycidyl compounds, as described for example in DE-C 24 10 513.

The hydroxyl-containing polyesters which are employed with particular preference have an OH functionality of greater than 2, an OH number of from 20 to 200 mg of KOH/g, preferably from 30 to 150 mg of KOH/g, a viscosity of less than 60,000 mPa·s, preferably less than 40,000 mPa·s, at 140°C and a melting point of from 70 to 120°C, preferably from 75 to 100°C.

Dicarboxylic acids which can be used in this process are all of the polycarboxylic acids listed below under 2. Monocarboxylic acids which are listed below under 3., for example, can likewise be employed.

Other preferred components are monomeric esters, for example bis(hydroxy(alcohol)) dicarboxylates, monocarboxylic esters of more-than-dihydric polyols, and oligo-
5 esters which can be prepared by condensation reaction from base materials which are customary in paint chemistry. Examples of compounds which can be regarded as such are:

1. Alcohols having 2 to 24 carbon atoms, preferably 2 to 10 carbon atoms, and 2 to 6 OH groups attached to
10 nonaromatic carbon atoms, for example ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butanediols, neopentylglycol, hexanediols, hexanetriols, perhydrobisphenol, dimethylolcyclohexane, glycerol, trimethylolethane,
15 trimethylolpropane, pentaerythritol, dipentaerythritol and mannitol;
2. Di- and polycarboxylic acids having 4 to 36 carbon atoms and 2 to 4 carboxyl groups, and esterifiable derivatives thereof, such as anhydrides and esters,
20 for example phthalic acid (phthalic anhydride), isophthalic acid, terephthalic acid, alkyltetrahydrophthalic acid, endomethylenetetrahydrophthalic anhydride, adipic acid, succinic acid, maleic acid, fumaric acid, dimeric fatty acids, trimellitic acid,
25 pyromellitic acid and azelaic acid;
3. Monocarboxylic acids having 6 to 24 carbon atoms, for example caprylic acid, 2-ethylhexanoic acid,

benzoic acid, p-tert-butylbenzoic acid, hexahydrobenzoic acid, monocarboxylic acid mixtures of natural oils and fats, such as coconut fatty acid, soya oil fatty acid, ricinenic fatty acid, hydrogenated and isomerized fatty acids, such as "Konjuvandol" fatty acid and mixtures thereof. It is also possible for the fatty acids to be employed as glycerides and to be reacted in transesterification and/or dehydration reactions;

- 10 4. Monohydric alcohols having 1 to 18 carbon atoms, for example methanol, ethanol, isopropanol, cyclohexanol, benzyl alcohol, isodecanol, nonanol, octanol and oleyl alcohol.

The polyesters can be obtained in a manner known per se by condensation in an inert gas atmosphere at temperatures of from 100 to 260°C, preferably from 130 to 220°C, in the melt or by an azeotropic procedure, as described for example in Methoden der Organischen Chemie (Houben-Weyl), Vol. 14/2, 1 - 5, 21 - 23, 40 - 44, Georg Thieme Verlag, Stuttgart, 1963 or in C.R. Martens, Alkyd Resins, 51 - 59, Reinhold Plastics Appl. Series, Reinhold Publishing Comp., New York, 1961.

Preferred acrylate resins which can be used as OH component are homo- or copolymers in which case, for example, the following monomers can be chosen as starting compounds: esters of acrylic acid and methacrylic acid with dihydric, saturated, aliphatic alcohols having 2 to

4 carbon atoms, for example 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 4-hydroxybutyl acrylate and the corresponding methacrylates; acrylic and methacrylic alkyl esters having 1 to 18 carbon atoms in the alcohol component, for example methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate and the corresponding methacrylates; cyclohexyl acrylate and cyclohexyl methacrylate; acrylonitrile and methacrylonitrile, acrylamide and methacrylamide; and N-methoxymethyl(meth)acrylamide.

Particularly preferred acrylate resins are copolymers of

- a) from 0 to 50% by weight of esters of acrylic or methacrylic acid with dihydric or polyhydric alcohols, such as 1,4-butanediol monoacrylate, hydroxypropyl (meth)acrylate; and also vinyl glycol, vinyl thioethanol, allyl alcohol and 1,4-butanediol monovinyl ether;
- b) from 5 to 95% by weight of esters of acrylic acid or methacrylic acid with monohydric alcohols containing 1 to 12 carbon atoms, such as methyl methacrylate, ethyl acrylate, n-butyl acrylate or 2-ethylhexyl acrylate;
- c) from 0 to 50% by weight of aromatic vinyl compounds such as styrene, methylstyrene or vinyltoluene;

- d) from 0 to 20% by weight of other monomers containing functional groups, for example acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, maleic anhydride, maleic monoesters, acrylamide, methacrylamide, acrylonitrile or N-methylol(meth)acrylamide and glycidyl (meth)acrylate, the proportion of group a) and/or b) being at least 5% by weight.

The acrylate resins can be prepared by the customary methods, i.e. by solution, suspension, emulsion or precipitation polymerization; however, they are preferably prepared by bulk polymerization, which can in turn be initiated by means of UV light.

Other polymerization initiators used are the customary peroxides or azo compounds, examples being dibenzoyl peroxide, tert-butyl perbenzoate or azodiisobutyronitrile. The molecular weight can be regulated with, for example, sulfur compounds, such as tert-dodecyl mercaptan.

Preferred polyethers can be prepared, for example, by polyaddition of epoxides, such as ethylene oxide, propylene oxide, butylene oxide, trimethylene oxide, 3,3-bis(chloromethyl)oxacyclobutane, tetrahydrofuran, styrene oxide, the 2,5-bis(epoxypropyl) ether of diphenylolpropane or epichlorohydrin with itself, for example in the presence of BF_3 , or by addition reaction of these epoxides, individually in a mixture or in succession,

with starting components containing reactive hydrogen atoms, such as alcohols or amines, for example water, ethylene glycol, 1,3- or 1,2-propylene glycol, pentamethylene glycol, hexanediol, decamethylene glycol, tri-
5 methylolpropane, 4,4'-dihydroxydiphenylpropane, aniline, ammonia, ethanolamine, ethylenediamine, di(β -hydroxypropyl)methylamine, di(β -hydroxyethyl)aniline, hydrazine and also hydroxyalkylated phenols, for example di(β -hydroxyethoxy)resorcinol.

10 It is likewise possible to employ hydroxyl-containing polyurethanes and/or polyureas.

The mixing ratio of the hydroxyl-containing polymers and the polyisocyanates according to the invention is generally chosen such that there are 0.5 - 1.2, preferably
15 0.8 - 1.1, NCO groups per OH group, with very particular preference 1.0 NCO group per OH group.

For the production of PU powder coatings, the isocyanate component is mixed with the appropriate hydroxyl-containing polymer and, if desired, catalysts and also pigments
20 and customary auxiliaries, such as fillers and leveling agents, for example silicone oil, acrylate resins, and the mixture is homogenized in the melt. This can take place in suitable apparatus, for example heatable kneading equipment, but preferably by extrusion, in which case
25 upper temperature limits of from 130 to 140°C should not be exceeded. The extruded composition, after cooling to room temperature and after appropriate comminution, is

ground to a ready-to-spray powder. The application of the ready-to-spray powder to suitable substrates can be carried out by the known methods, for example by electrostatic powder spraying, fluidized-bed sintering, or
5 electrostatic fluidized-bed sintering. Following application of the powder, the coated workpieces are heated for curing purposes for from 4 to 60 minutes at a temperature of from 150 to 220°C, preferably for from 6 to 30 minutes at from 160 to 200°C.

10 The subject-matter of the invention is illustrated in more detail below with reference to examples. The abbreviations used are explained in the description at the appropriate points (pages 3 and 4).

A Preparation of the hydroxyl and uretdione group-
15 containing polyisocyanates according to the inven-
tion

A 1 Polyol chain extenders

General preparation procedure

The starting components - cf. Tables 1 and 2 - are
20 placed in a reactor and heated with the aid of an oil bath to $\approx 140^{\circ}\text{C}$. After the substances have been largely melted, 0.1% by weight of di-n-butyltin oxide is added as catalyst. Initial elimination of
25 water takes place at from 150 to 160°C. The temperature is raised to from 180 to 190°C over the course

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5 of from 2 to 3 hours and the esterification is brought to an end over a further 8 to 10 hours. During the entire reaction period, the bottom product is stirred and a weak stream of nitrogen is passed through the reaction mixture. The acid number of the polyesters is always less than 2 mg of KOH/g.

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A.1.1.1

Table 1: Polyol chain extenders (component D) - A 1.1.1; functionality: F = 2

Example A 1.1.1.	Starting components in mol					Characteristics	
	As	Sb	N	P	HD	OH number [mg of KOH/g]	Viscosity 25°C [mPa·s]
1	1	-	2	-	-	335 ± 15	≈ 1500
2	-	1	2	-	-	289 ± 10	≈ 1150
3	Polycaprolactones Interox-Capa* 200					216	Melting range 18 - 23°C
4	Polycaprolactone Interox-Capa* 210					112	Melting range 30 - 40°C

As: adipic acid

Sb: sebacic acid

N : neopentyl glycol

P : 1,5-pentanediol

HD: 1,6-hexanediol

* : Trade-mark

A 1.2

Table 2: Polyol chain extenders (component D); functionality: F ≥ 3

Example	Starting components in mol				Characteristics	
	As	N	HD	TMP	OH number [mg of KOH/g]	Viscosity 25°C [mPa·s]
1	2	1	1	1	270 - 285	5500
2	Polycaprolactones Interox-Capa* 305				305 - 320	1350
3	Polycaprolactones Interox-Capa* 316				210 - 220	2300

As: adipic acid

N : neopentyl glycol

HD: 1,6-hexanediol

TMP: trimethylolpropane

* : Trade-mark

A 2 Polyisocyanates containing hydroxyl and uretdione groups

General preparation procedures

A 2.1 With solvent

5 The polyol component - cf. Table 3 - and the catalyst (0.03 - 0.5% by weight DBTL) are introduced into the reactor as a solution in the solvent. With vigorous stirring and under an inert gas atmosphere, the calculated quantity of
10 uretdione, as a solution in the solvent, is added rapidly at a rate such that the reaction temperature does not exceed 100°C. The reaction is monitored by means of titrimetric NCO determination and is over after 1 to 3 hours. The solvent
15 is subsequently removed, and the product is cooled and, if desired, comminuted.

A 2.2 Without solvent

20 The uretdione was fed at a temperature of from 60 to 110°C into the entry barrel of a twin-screw extruder, the polyol component - cf. Table 3 - being metered in simultaneously at a temperature of from 25 to 110°C. The uretdione and/or the polyol component contained, if appropriate, the quantity of catalyst required - from 0.03 - 0.5%
25 by weight DBTL -, based on the end product.

5 The extruder employed is composed of ten barrels,
of which five are heating zones. The temperatures
of the heating zones are within a wide range -
between 50 and 190°C - and can be controlled
individually. All temperatures are setpoint
temperatures, and regulation in the barrels takes
place by electric heating and pneumatic cooling.
The die element is heated by an oil thermostat.
The rotary speed of the twin screw, fitted with
10 conveying elements, was between 50 and 380 rpm.

The reaction product, obtained at a rate of from
10 to 130 kg/h, is either cooled, then comminuted
or shaped and bagged, or else the melt itself is
shaped, cooled and bagged.

15 The physical and chemical characteristics of the
novel process products and the molar compositions
are collated in Tables 3 to 5.

The uretdiones prepared by known processes had
the following characteristics:

20 IPDI uretdione

NCO-free: from 16.8 to 18.5% by weight

Total NCO: from 37.4 to 37.8% by weight

DI 51 uretdione

NCO-free: from 20.1 to 21.2% by weight

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- 24 -

O.Z. 5002

Total NCO: from 43.7 to 44.9% by weight

HDI uretdione (DESMODUR® N 3400)

NCO-free: from 20.9 to 22.1% by weight

Total NCO: from 35.6 to 36.5% by weight

Table 3: Polyisocyanates containing hydroxyl and uretdione groups

Ex.	Composition in mol				Chemical and physical characteristics			
	Uretdio ne comp. A	Polyol comp. B	Diol(s)) comp. C	Chain extenders component D	NCO content [% by wt.]		Melting range [°C]	Glass transition temperature [°C]
A 2	IPDI			F = 2	F ≥ 3	free	total	
1	3	TMP (1)	E (3)	-	-	0	8.4	122 - 125
2	3	TMP (1)	B (3)	-	-	0	8.4	113 - 117
3	3	TMP (1)	HD (3)	-	-	0	8.1	94 - 97
								87 - 106
								55 - 69
								56 - 60

E : ethylene glycol

B : 1,4-butanediol

HD : 1,6-hexanediol

TMP: trimethylolpropane

4	3	TMP (1)	N (3)	-	0	7.1	125 - 128	90 - 105
5	3	TMP (1)	Pm (3)	-	0	7.3	109 - 116	61 - 85
6	3	TMP (1)	T (3)	-	0	7.2	98 - 101	49 - 70
7	3	TMP (1)	Eg (3)	-	0	6.3	106 - 109	65 - 84
8	3	TMP (1)	TEG (3)	-	0	6.6	88 - 91	43 - 58
9	3	TMP (1)	B (2.5)	A 1.1.1 (0.5)	0	7.7	98 - 101	46 - 71

N : neopentylglycol
 Pm : 3-methyl-1,5-pentanediol
 T : 2,2,4(2,4,4)-trimethylhexanediol
 Eg : neopentylglycol hydroxypivalate
 TEG : triethylene glycol
 B : 1,4-butanediol

Table 3: Continued

Ex.	Composition in mol					Chemical and physical characteristics			
	Uretdio ne comp. A	Polyol comp. B	Diol(s)) comp. C	Chain extenders component D		NCO content [% by wt.]		Melting range [°C]	Glass transition temperature [°C]
A 2	IPDI			F = 2	F ≥ 3	fre	total		
10	3	THEIC(1)	N (2.5)	A 1.1.2 (0.5)	-	0	7.2	103 - 107	50 - 73
11	3	TMP (1)	B (2.5)	A 1.1.3 (0.5)	-	0	7.4	80 - 83	35 - 57
12	3	TMP (1)	E (2)	A 1.1.3 (1)	-	0	6.5	76 - 79	36 - 56
13	3	TMP (1)	B (2)	A 1.1.3 (1)	-	0	6.7	79 - 82	38 - 59

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14	3	TMP (1)	E (2.5)	A 1.1.4 (0.5)	-	0	6.8	78 - 81	36 - 53
15	3	THRIC(1)	B (2.5)	A 1.1.4 (0.5)	-	0	6.1	85 - 88	39 - 59

Table 4: Polyisocyanates containing hydroxyl and uretdione groups

Ex.	Composition in mol					Chemical and physical characteristics			
	Uretdione comp. A	Polyol comp. B	Diol(s) comp. C	Chain extenders component D		NCO content [% by wt.]	Melting range [°C]	Glass transition temperature [°C]	
				P = 2	P ≥ 3				
	IPDI					free	total		
1	3		B (3)	-	A1.2.1(1)	0	6.4	78 - 81	41 - 59
2	3		N (3)	-	A1.2.1(1)	0	6.2	80 - 83	52 - 63
3	3		E (3)	-	A1.2.2(1)	0	7.1	73 - 77	24 - 43
4	3		B (3)	-	A1.2.2(1)	0	6.9	69 - 72	22 - 42
5	3		Pm (3)	-	A1.2.2(1)	0	6.6	62 - 65	21 - 39
6	4		B (4)	-	A1.2.3(1)	0	6.3	71 - 74	23 - 41
7	4		N (4)	-	A1.2.3(1)	0	6.2	73 - 75	26 - 40
8	5		E (5)	-	A1.2.3(1)	0	7.4	97 - 101	51 - 66
9	5		B (5)	-	A1.2.3(1)	0	7.3	94 - 97	45 - 65

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10	3.5	TMP(0.5)	B (2) HD(1.5)	-	A1.2.3(0. 5)	0	7.0	88 - 91	39 - 54
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Table 5: Polyisocyanates containing hydroxyl and uretdione groups

Ex.	Composition in mol					Chemical and physical characteristics			
	Uretidion e comp. A	Polyol comp. B	Diol(s) comp. C	Chain extenders component D		NCO content [% by wt.]		Melting range [°C]	Glass transition temperature [°C]
A 2	IPDI/DI 51			P = 2	P ≥ 3	fre	total		
1	2 1	TMP(1)	E(3)	-	-	0	8.7	84 - 87	28 - 46
2	1 2	TMP(1)	E(3)	-	-	0	9.5	52 - 55	12 - 27
3	2 1	TMP(1)	B(3)	-	-	0	7.9	81 - 84	25 - 42
4	1 2	TMP(1)	B(3)	-	-	0	8.8	56 - 59	9 - 25
5	1.5 1.5	TMP(1)	N(3)	-	-	0	8.9	83 - 87	27 - 43
6	2.5 0.5	TMP(1)	B(2.5)	A1.1.1(0.5)		0	8.0	84 - 86	28 - 42
7	2.5 1	TMP(0.5	B(3.5)	-	A1.2.3(0.5)	0	7.1	60 - 65	15 - 37
8	4 1	-	E(5)	-	A1.2.3(1)	0	8.3	68 - 72	24 - 43

Table 5 - Continued

Ex.	Composition in mol					Chemical and physical characteristics			
	Uretdio ne comp. A	Polyol comp. B	Diol(s) comp. C	Chain extenders component D		NCO content [% by wt.]	Melting range [°C]	Glass transition temperature [°C]	
				P = 2	P ≥ 3				
A 2	IPDI/HD I								
9	2.5 0.5	TMP (1)	B(3)	-	-	0	96 - 99	47 - 69	
10	2 1	TMP (1)	E(3)	-	-	0	92 - 95	38 - 61	
11	2 1	TMP (1)	B(3)	-	-	0	85 - 88	36 - 60	
12	1.5 1.5	TMP (1)	E(3)	-	-	0	79 - 84	31 - 49	
13	2.5 0.5	TMP (1)	B(2.5)	A1.1.3(0.5)	-	0	70 - 75	31 - 52	
14	4.5 0.5	-	B(5)	-	A1.2.3(1)	0	71 - 74	32 - 55	

B Polyesters

Table 6 below contains examples relating to the polyesters which are commercially available for formulating PU powder coatings.

Table 6

Example	Producer Country	Name	Chemical and physical characteristics				
			OH number [mg of KOH/g]	Acid number [mg of KOH/g]	Melting range [°C]	Glass trans- ition temp. [°C]	Viscosity at 160°C [mPa·s]
B							
1	Hoechst AG Italy	ALFTALAT AN 739	55 - 60	2 - 4	82 - 90	> 50	24 - 29,000
2	DSM Netherlands	URALAC B 1460	38 - 41	4 - 4.5	70 - 75	50	40,000
3	UCB Belgium	CRYLCOAT 240	26 - 31	3 - 4	74 - 80	> 50	33 - 38,000

C Polyurethane powder coatingsGeneral preparation procedure

5 The comminuted products - polyisocyanates containing uretdione groups (crosslinking agents), polyesters, leveling agent masterbatch and, if appropriate, catalyst masterbatch - are intimately mixed with or without the white pigment in an edge runner mill and then homogenized in an extruder at a maximum temperature of 130°C. After cooling, the extrudate is
10 fractionated and ground with a pinned-disk mill to a particle size less than 100 µm. The powder thus prepared is applied with an electrostatic power spraying unit at 60 kV to degreased, optionally pretreated iron panels which are baked in a convection oven at
15 temperatures between 160 and 200°C.

Leveling agent masterbatch

10% by weight of the leveling agent - a commercially available copolymer of butyl acrylate and 2-ethylhexyl acrylate - are homogenized in the melt in the
20 corresponding polyester and comminuted after having solidified.

Catalyst masterbatch

5% by weight of the catalyst - DBTL - are homogenized in the melt in the corresponding polyester and
25 comminuted after having solidified.

The abbreviations in the tables which follow have

the following meanings:

	CT	= coat thickness in μm	
	EI	= Erichsen indentation in mm	(DIN 53 156)
	CH	= cross-hatch test	(DIN 53 151)
5	GG 60° *	= Gardner gloss measurement	(ASTM-D 5233)
	Imp. rev.	= Impact reverse in g·m	
	HK	= König hardness in sec	(DIN 53 157)

C 1 Pigmented powder coatings

Table 7:

Exempl e C1 Formulation	1	2'	3	4	5	6	7	8''	9	10	11''	12
Crosslinking agent acc. A.2	33.6 9	28.9 (1)	21.4 7	29.3 8	24.1 (5)	37.2 1	35.6 6	30.72 (9)	30.44 (9)	36.57 (11)	31.57 (11)	26.3 1
Table 3 Ex. ()	(1)		(2)	(3)		(6)	(9)					(12)
Polyester acc. to B 1	66.3 1	71.1	-	-	-	62.7 9	64.3 4	69.28	-	63.43	68.43	-
Polyester acc. to B 2	-	-	-	70.6 2	-	-	-	-	69.56	-	-	-
Polyester acc. to B 3	-	-	78.5 3	-	75.9	-	-	-	-	-	-	73.6 9
Notes	All formulations contain 40% by weight of TiO ₂ (white pigment) and 0.5% by weight each of leveling agent and benzoin; the OH/NCO ratio is 1:1; "											
	OH/NCO = 1:0.8											

C 1 Pigmented powder coatings

Table 8:

Exempl e C1 Formulation	13	14"	15	16	17	18"	19	20	21	22	23	24"
Crosslinking agent acc. A.2	40 (1)	34.7 9 (1)	26.6 1 (1)	32.1 8 (3)	38.2 1 (4)	35.7 6 (4)	32.8 1 (4)	25.17 (4)	33.80 (5)	36.89 (9)	37.88 (10)	32.7 8 (10)
Table 4 Ex. ()												
Polyester acc. to B 1	60	65.2 1	-	-	61.7 9	64.2 4	-	-	-	63.11	62.12	67.2 2
Polyester acc. to B 2	-	-	-	67.8 2	-	-	67.1 9	-	66.20	-	-	-
Polyester acc. to B 3	-	-	73.3 9	-	-	-	-	74.83	-	-	-	-
Notes	All formulations contain 40% by weight of TiO ₂ (white pigment) and 0.5% by weight each of leveling agent and benzoin; the OH/NCO ratio is 1:1; "											
	OH/NCO = 1:0.8											

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Coating data																	
CT	81- 95	73- 87	67- 78	71- 83	59- 76	63- 71	67- 75	71-84	65-77	62-77	84-94	74- 84					
GG 60° *	89/9 0	90	91	89	88/8 9	90	89/9 0	91	89/90	83/85	91/92	90/9 1					
CH	0	0	0	0	0	0	0	0	0	0	0	0					
EI	> 10	> 10	9.5/ 10	10	> 10	> 10	> 10	9.9/1 0	10	> 10	> 10	> 10					
Imp. rev.	> 944	806. 4	806. 4	806. 4	> 944	> 944	806. 4	806.4	944	460.8	> 944	>					
Notes	Curing conditions: 200°C/8 to 10 minutes, 180°C/15 minutes or 170°C/25 minutes																

C 1 Pigmented powder coatings

Table 9:

Exempl e C1 Formulation	25	26	27	28 ¹⁾	29	30 ¹⁾	31	32	33	34	35	36
Crosslinking agent acc. A.2	32.9	19.6	35.0	30.1	29.9	25.4	22.7	27.68	34.79	37.54	24.64	25.1
Table 5 Ex. ()	1 (1)	3 (2)	7 (3)	7 (3)	(3)	(3)	1 (3)	(4)	(6)	(9)	(9)	7 (13)
Polyester acc. to B 1	67.0	-	64.9	69.8	-	-	-	-	65.21	62.46	-	-
Polyester acc. to B 2	-	-	3	3	70.1	74.6	-	72.32	-	-	-	-
Polyester acc. to B 3	-	80.3	-	-	-	-	77.2	-	-	-	75.36	74.8
Notes	All formulations contain 40% by weight of TiO ₂ (white pigment) and 0.5% by weight each of leveling agent and benzoin; the OH/NCO ratio is 1:1; ¹⁾ OH/NCO = 1:0.8											
		7					9					3

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C 2 Transparent powder coatings

The process described was also used to prepare the transparent powder coatings, to apply them and to bake them at between 200 and 170°C.

Table 10

Example C2 Formulation	1	2	3	4	5	6	7
Crosslinking agent acc. A.2	35.66 (9)	23.16 (9)	36.57 (11)	40.0	25.17 -	35.07	24.64
Table 3 Ex. ()	-	-	-	(1)	(4)	-	-
Table 4 Ex. ()	-	-	-	-	-	(3)	(9)
Table 5 Ex. ()	-	-	-	-	-	-	-
Polyester acc. to B 1	64.34	-	63.43	60.0	-	64.93	-
Polyester acc. to B 3	-	76.84	-	-	74.83	-	75.36
Notes	All formulations contained 0.5% by weight each of leveling agent and benzoin and also 0.1% by weight of DBTL; the OH/NCO ratio is 1:1						
Coating data							
CT	55-67	51-70	60-72	59-70	57-73	62-74	58-69
HK	204	197	209	189	194	181	193
CH	0	0	0	0	0	0	0
EI	> 10	> 10	> 10	> 10	> 10	> 10	> 10
Notes	Curing conditions: 200°C/6 - 8 minutes, 180°C/12 - 15 minutes or 170°C/20 - 25 minutes						

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A polyaddition product containing hydroxyl groups and uretdione groups, and being formed essentially of:
 - A) from 55 to 85% by weight of a uretdione derived from a diisocyanate, and at least one hydroxyl compound selected from the group consisting of:
 - B) from 2 to 15% by weight of a polyol having at least 3 hydroxyl groups,
 - C) from 5.5 to 31% by weight of a diol, and
 - D) from 7.5 to 33% by weight of a chain extender having a functionality of from 2 to 6,provided that when the polyol B) is not contained, then the chain extender D) having a functionality of 3 to 6 must be contained, wherein the polyaddition product carry terminal hydroxyl groups and have a functionality of at least 3, a molecular weight between 1,500 and 4,400 and a free isocyanate content of less than 0.5% by weight.
2. A polyaddition product as claimed in claim 1, which has a functionality of from 3 to 4 and a molecular weight between 1,800 and 3,500.
3. A polyaddition product as claimed in claim 1 or 2, wherein the uretdione is of at least one diisocyanate selected from the group consisting of hexamethylene 1,6-diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 2,2,4(2,4,4)-

trimethylhexamethylene diisocyanate and isophorone diisocyanate.

4. A polyaddition product as claimed in any one of claims 1 to 3, wherein the polyol is at least one member selected from the group consisting of glycerol, trimethylolpropane, ditrimethylolpropane, trimethylolethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β -hydroxyethyl) isocyanurate, pentaerythritol, mannitol and sorbitol.
5. A polyaddition product as claimed in any one of claims 1 to 4, wherein the diol is at least one member selected from the group consisting of ethylene glycol, triethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentylglycol, 2,2,4(2,4,4)-trimethylhexanediol (isomeric mixture) and neopentylglycol hydroxypivalate.
6. A polyaddition product as claimed in any one of claims 1 to 5, wherein the chain extender is a linear hydroxyl-terminated polyester or polycaprolactone having a molecular weight between 180 and 2,000 and a hydroxyl number between 625 and 50 mg of KOH/g.
7. A polyaddition product as claimed in claim 6, wherein the linear hydroxyl-terminated polyester is derived from at least one diol selected from the group consisting of ethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 2,2,4(2,4,4)-trimethylhexanediol,

neopentylglycol hydroxypivalate, 2-methylpropanediol, 2,2-dimethylpropanediol, diethylene glycol, 1,12-dodecanediol and trans- and cis-cyclohexanedimethanol and at least one dicarboxylic acid selected from the group consisting of succinic, adipic, suberic, azelaic, sebacic and 2,2,4(2,4,4)-trimethyladipic acid (isomer mixture), or is derived from ϵ -caprolactone or hydroxycaproic acid.

8. A polyaddition product as claimed in any one of claims 1 to 5, wherein the chain extender is a branched polyester or polycaprolactone having a functionality of at least 3, a molecular weight between 210 and 2,000 and a hydroxyl number between 900 and 100 mg of KOH/g.
9. A polyaddition product as claimed in claim 8, wherein the chain extender comprises in addition to a dicarboxylic acid, hydroxycarboxylic acid or lactone, at least one mol of a polyol selected from the group consisting of trimethylol-ethane, trimethylolpropane, tris(hydroxyethyl) isocyanurate and pentaerythritol.
10. A polyaddition product as claimed in any one of claims 1 to 5, wherein the chain extender is based on ϵ -caprolactone or a hydroxycaproic acid.
11. A polyaddition product as claimed in any one of claims 1 to 5, wherein the chain extender is a linear or branched hydroxyl-terminated polyester having a hydroxyl functionality of 2 to 6, a molecular weight of 180 to 2,000 and a hydroxyl number of 900 to 50 mg of KOH/g.

12. A polyaddition product as claimed in any one of claims 1 to 11, wherein the chain extender has a functionality of from 2 to 4.

13. A process for preparing the polyaddition product as claimed in any one of claims 1 to 12, which comprises:

reacting the uretdione derived from a diisocyanate A with at least one of the hydroxyl-containing reactants B, C and D, provided that when the polyol B is not employed, then the chain extender having a hydroxyl functionality of 3 to 6 must be employed.

14. A process for preparing the polyaddition product as claimed in any one of claims 1 to 12, which comprises:

reacting the uretdione A having terminal isocyanate groups and being derived from a diisocyanate, with a mixture of the polyol B, the diol C and the chain extender D,

wherein the mixture contains at least 1 mol of the polyol B or the chain extender D having three to six hydroxyl groups per molecule relative to 3 mols of the uretdione A; and the uretdione A, the polyol B, the diol C and the chain extender D are employed in such amounts that the resulting polyaddition product has a functionality of at least 3.

15. The process as claimed in claim 13 or 14, wherein the reaction is carried out at a temperature of from 50 to 100°C in a solvent which is removed after the reaction has taken place.

16. The process as claimed in claim 13 or 14, wherein the reaction is carried out without solvent in an intensive kneading apparatus at a temperature of from 110 to 190°C.
17. The process as claimed in claim 16, wherein the reaction is carried out in a twin-screw extruder.
18. The process as claimed in any one of claims 13 to 16, wherein a catalyst is employed for the reaction in a concentration of from 0.01 to 1% by weight, based on the starting materials employed.
19. The process as claimed in claim 18, wherein an organic tin compound is employed as the catalyst.
20. The process as claimed in claim 18 or 19, wherein from 0.03 to 0.5% by weight of the catalyst is employed.
21. An elimination-free, transparent or pigmented polyurethane powder coating, which comprises the polyaddition product as claimed in any one of claims 1 to 12, in combination with a hydroxyl-containing polymer.
22. A polyurethane powder coating as claimed in claim 21, which is based on an OH/NCO ratio of from 1:0.5 to 1.2.
23. A polyurethane powder coating as claimed in claim 21 or 22, which also contains a catalyst in a concentration of from 0.03 to 0.5% by weight, including a catalyst which may be employed in the production of the polyaddition product.

24. A polyurethane powder coating as claimed in claim 23, wherein an organic tin compound is contained as the catalyst.
25. A polyurethane powder coating as claimed in claim 23 or 24, wherein from 0.05 to 0.15% by weight of the catalyst is contained.
26. A polyurethane powder coating as claimed in any one of claims 21 to 25, wherein the hydroxyl-containing polymer is a polyester having a functionality of greater than 2, an OH number of from 20 to 200 mg of KOH/g, a viscosity of less than 60,000 mPa·s at 160°C and a melting point of from 70 to 120°C.
27. A polyurethane powder coating as claimed in claim 26, wherein the polyester has a functionality of greater than 2, an OH number of from 30 to 150 mg of KOH/g, a viscosity of less than 40,000 mPa·s at 160°C and a melting point from 75 to 100°C.
28. A method of coating a substrate according to any one of claims 21 to 27, which comprises:
- applying the powder coating composition to a substrate,
- and
- curing the so-applied powder coating composition at a temperature of 160 to 200°C for from 4 to 60 minutes, wherein the substrate is one which can withstand the curing conditions.
29. A polyaddition product having terminal hydroxyl groups and uretdione groups, and being formed essentially of:

A) from 55 to 85% by weight of a uretdione which is derived from a diisocyanate and has terminal isocyanate groups,

B) from 2 to 15% by weight of a polyol having at least hydroxyl groups,

C) from 5.5 to 31% by weight of a diol, and

D) from 7.5 to 33% by weight of a chain extender having a functionality of 2 to 6, wherein the polyaddition product has a functionality of at least 3, a molecular weight of between 1,500 and 4,400 and a free isocyanate content of less than 0.5% by weight.

30. A polyaddition product as claimed in claim 29, wherein the chain extender is a linear or branched hydroxyl-terminated polyester having a hydroxyl functionality of 2 to 6, a molecular weight of 180 to 2,000 and a hydroxyl number of 900 to 50 mg of KOH/g.

31. A polyaddition product as claimed in claim 29 or 30, which has a functionality of from 3 to 4 and a molecular weight of between 1,800 and 3,500.

FETHERSTONHAUGH & CO.

OTTAWA, CANADA

PATENT AGENTS